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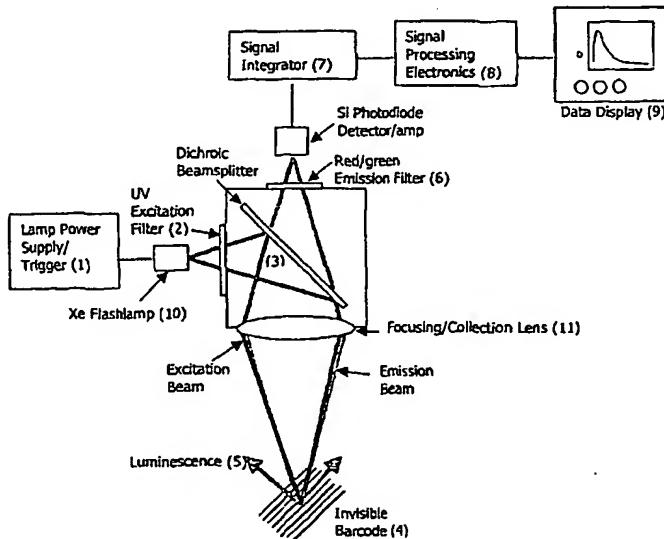
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[Continued on next page]

(54) Title: SYSTEM AND METHODS FOR PRODUCT AND DOCUMENT AUTHENTICATION



WO 03/105075 A1

(57) Abstract: The present invention relates to both a system and method for product and document authentication. The system used herein comprises one or more inks, at least one of which is either invisible to the naked eye or is fluorescent or luminescent, an optical (2, 3, 8) scanning component capable of detecting the signals emitted by all of said inks, and an information technology component for analyzing said signals. Given the large number of combinations of dyes, sizes and shapes of the markings made with said dyes, the ability to change the type, size and shape for the marking (5) for a given product, and the ability to keep track of the dyes and markings used for a given product, the system allows a nearly foolproof system for product authentication. The method involves the above system, or other combinations of inks, for authenticating a given product.

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TITLE OF THE INVENTION

System and Methods for Product and Document Authentication

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CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Patent Application Serial No. 09/354,891, filed July 16, 1999,
10 which is incorporated in its entirety herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
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N/A

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BACKGROUND OF THE INVENTION

Accurate verification of products and documents is critical to a wide variety of industries including the manufacture of pharmaceuticals, clothing, or automotive parts, and the issuance of credit and identification cards or travel/immigration documentation. Counterfeitors of products, currency and documents have developed increasingly sophisticated methods of detection and copying of marks and labels. Counterfeiting and diversion cost owners of products, brand names, and intellectual property billions of dollars annually on a world-wide basis, according to the International Anti-Counterfeiting Council (IACC). The problem in the United States, for example, encompasses an estimated loss in revenues of \$
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al., Method for Tagging Petroleum Products) Of particular relevance to the present invention is prior art in which bar codes are enabled for security purposes using luminescent invisible inks. (5,542,971, J. D. Auslander and W. Berson,
5 Bar Codes Using Luminescent Invisible Inks; 5,502,304, W. Berson and J. D. Auslander, Bar Code Scanner for Reading a Visible Ink and a Luminescent Invisible Ink and 5,525,798, W. Berson and J.D. Auslander, Bar Code Scanner for Reading a Lower Layer Luminescent Invisible Ink that is Printed below
10 an Upper Layer Luminescent Invisible Ink)

Specific use of lanthanide chelates as security marking is taught in 5,837,042 (B. A. Lent, et al., Invisible Fluorescent Jet Ink), a patent in which lanthanide chelates comprised of the ligands of the 1,3-diketone class or
15 salicylic acid are utilized in ink jet printing applications that feature covert marking.

Unlike most other luminescent organic or organometallic compounds whose lifetime for spontaneous emission (fluorescence) appears commonly in the 1-30 nanosecond range
20 (corresponding to the time required for signal decay to $1/e$, for single exponential decays), the lanthanide chelates display luminescence that is measured in the 0.1 - 5.0 millisecond (ms) time domain. These measurements are carried out using time-resolved emission techniques in which
25 a pulsed source of light is used to excite a sample (J. N. Demas, Excited State Lifetime Measurements, Academic Press, New York, 1983).

The capabilities of rare earth chelates to produce bright luminescence that displays a long decay time have
30 been chiefly exploited in the assay of biological macromolecules. For example, the tagging of antigen or

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In the field of security bar coding, lanthanide chelate luminescence has been employed, along with scanning devices capable of distinguishing long-lived luminescence have also been reported. (5,542,971, J. D. Auslander and W. Berson,
5 Bar Codes Using Luminescent Invisible Inks; 5,693,693, J. D. Auslander and W. Berson, Bar Code Printing and Scanning Using Wax-based Invisible Fluorescent Inks) A recent patent describes a method in which light signals from a luminescent bar code layer doped with a phosphorescent ink are
10 distinguished, based on time resolution, from the faster decay of fluorescent light emanating from a conventional film layer (5,861,618, W. Berson, System and Method of Improving the Signal to Noise Ratio of Bar Code and Indicia Scanners that Utilize Fluorescent Inks).

15

BRIEF SUMMARY OF THE INVENTION

The present invention relates to both a system and method for product authentication. The system used herein
20 comprises (1) one or more dyes or pigments, at least one of which is either invisible to the naked eye or is fluorescent or luminescent, (2) an optical component capable of detecting the signals emitted by all of said inks, and (3) an information technology component for analyzing said
25 signals. There are a large number of combinations of (1) dyes or pigments, (2) sizes and shapes of the markings made with said dyes, (3) the ability to change the type, size and shape for the marking for a given product, and (4) the ability to keep track of the dyes and markings used for a
30 given product. With these features the system allows a nearly foolproof method for product authentication. The

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Figure 10 shows system data collection, routing and transmission modes.

Figure 11 shows a block diagram of the overall system including mark illumination, detection and data 5 transmission.

Figure 12 shows an illustration of an on-line reader for reading authentication of variable data signatures and data transmission capability.

Figure 13 shows a block diagram of a generic two-10 channel detection device covered by this invention.

Figure 14 shows a sequence of luminescence spectra and recorded lifetimes during the course of heat treatment for two europium chelates (I and II), one of which is heat labile and one relatively heat-stable. The times range from 15 0.45 (spectrum a) through 1.12 (spectrum d) milliseconds in the heat treatment process.

Figure 15 shows luminescence spectra for two near-infrared dyes recorded before (solid lines) and after (dashed lines) irradiation treatment using a Xenon lamp.

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DETAILED DESCRIPTION OF THE INVENTION

A system for product authentication is described that integrates unique luminescent or fluorescent tags (also 25 referred to as taggants) with an optical scanning system and information technologies. (These tags are otherwise referred to as dyes, pigments, inks, marks, or labels elsewhere in this application.) Some tags are the subject of a pending patent application (U.S. Serial No. 09/354,891, 30 filed 7/16/99, hereafter referred to as '891), which is incorporated herein in its entirety. This application

classes of structures include 1,5-diphenyloxazole and thianthrene (Figure 2).

Several possible embodiments of the optical scanning system and its subsystems/components are described. The 5 scanner will provide an indication to the user as to (1) whether it detects a tag; and (2) whether or not a detected tag is authentic. By linking the scanner to a database system - or otherwise incorporating such a capability into the scanner itself - this authentication will be based upon 10 the most up-to-date information regarding the tag(s) in use. Further, the authentication can be linked to an inventory control and management system, providing even greater benefit to the user.

Some features of the dyes used herein will be briefly 15 discussed herein, although '891 should be referred to for additional information. The design of the ligand chromophores for rare earth chelates has been limited historically to the basic requirements of UV absorption (improved light harvesting) and ligand-metal excited state 20 energy matching. We demonstrate in '891 that ligands having a particular assembly of substituent groups can be used in a predictable way in order to act as more effective sensitizing agents.

The effect of adding a charge transfer (CT) feature to 25 the local ligand transition is shown in Table 1, which illustrates absorption and luminescence data for the europium compounds shown in Figure 1. Listed are wavelengths for absorption by the free ligand in a common solvent as well as the peak wavelength and peak extinction 30 coefficient for the corresponding Eu chelates. Additional data are provided that show the expected luminescence

longer wavelength of the peak absorption for compounds 2, 3 and 4 vs 1 in Table 1). (Also compare luminescence data for compound 6 vs. compound 5.) This wavelength region is appropriate for use in conjunction with a number of 5 different light sources (e.g., Hg lamps) but in particular these wavelengths match light sources that include ultraviolet light emitting diodes (LED's). The latter are increasingly available and provide narrow band excitation at low cost and high efficiency. Yet another feature is that 10 chelates taken together, or a single chelate that is comprised of a combination of different ligands (for example, three ligands coordinated to a lanthanide ion, Ln(XYZ)) will harvest light (broad band excitation) more effectively (e.g., ligands for 1 and 4 taken together).

15 To facilitate understanding of the invention, a number of terms are defined.

The term "luminescence" refers to emitted radiation that results from deexcitation of a molecule or ion from an excited electronic state to its ground electronic state. 20 The emitted radiation is referred to as fluorescence if the excited and ground electronic states are of the same spin multiplicity (de-excitation does not require a change in spin angular momentum); the emitted radiation is known as phosphorescence if de-excitation is "spin forbidden" and 25 requires a change in spin angular momentum. Luminescence is a process that normally requires the absorption of light at one wavelength, resulting in excited species which are fluorescent or phosphorescent at a different (usually longer) wavelength; R.S Becker, "Theory and Interpretation 30 of fluorescence and Phosphorescence," Wiley-Interscience, pages 76-97, New York, 1969.

decay curve. Most commonly, a luminescence decay will follow an exponential function; however, the decay pattern may be more complex, reflecting the possible array of compositions that display different properties of the 5 composition, or different physical environments. More complex decay functions that can be shown to fit an observed luminescence decay pattern include multiple exponentials (double, triple, etc.), a "stretched exponential", a Gaussian distribution of exponentials, or other complex 10 functions, J.N. Demas, *supra*.

The decay time (τ or $1/e$ for an exponential function), as it is defined, is a characteristic of the luminescence compositions of the present invention. In one embodiment, luminescence from a marked substrate will follow a single 15 exponential decay. In the accompanying Figure 4, the luminescence of chelate 4 (described in Table 1) is shown, along with the identification of the material that is marked and the experimental conditions used for observation. The parameters associated with this embodiment are (a) the 20 intensity profile (Fig 4), (b) the log plot of intensity vs. time that is a linear function for a single exponential decay, and (c) a luminescence lifetime (having the symbol, τ) that results from the slope of the log plot or from other curve fitting procedures. Typical decay constants (τ) for 25 lanthanide chelates, and a variety of other metal complexes in general, commonly fall in the time domain of 1 microsecond to 1 second, depending upon environmental conditions.

In other embodiments, luminescence follows a decay 30 pattern that is described best by two exponentials. The double exponential behavior can be illustrated with a log

in the present specification) of a sample containing a luminescent compound. Examples of luminescence lifetime modifiers include, but are not limited to, imidazole, analogs of imidazole, derivatives of imidazole, alkene polymers, polyesters, biopolymers, carboxylic acids, ketones, amides, phosphine or pyridine oxides, or polymers that provide coordination sites for metals including poly(vinyl acetate) and poly(vinylpyrrolidinone). The term "luminescence enhancer" refers to a luminescence lifetime modifier that enhances the luminescence of a luminescent compound when tested under the conditions described herein.

The term "substrate" as used herein, refers to a material having a rigid or semi-rigid surface. Such materials will preferably take the form of either organic or inorganic materials, such as paper (e.g. colored, plain, currency, bank notes, stocks, bonds), plastic, leather, cloth, thread, metal, and glass, or other convenient forms may be used. Other substrates may include plastic label stock, plastic card stock, metal or plastic foils, holographic foils and materials and adhesive layers associated with labels. In some embodiments, at least one surface of the substrate will be substantially flat. Other types of materials that can be usefully doped or tagged include sprays, adhesives, or films and coatings. A substrate may be marked, labeled, tagged or otherwise designated or sorted as the result of application of a luminescent composition of the present invention.

The term "metal" as used herein, refers to a metal center, a metal ion, or a metallic element, without regard to any specific oxidation state.

information can be detected using a scanning device that can store or transmit data for recovery and use in the verification of product or document identity. The technology is enabled through the use of, for example, 5 metal chelates that show discrete luminescence signals whose decay times are an adjustable variable that depends on the selected metal, the chelating ligand, and modifying agents that provide further control over luminescence lifetime. Two or more chelates may be used in combination to provide a 10 decay time profile that can reflect a weighted average of the two respective decay constants (τ_1 and τ_2) or appear in two time domains that are discriminated.

Luminescent compositions are identified that provide a means of marking a substrate, using luminescence decay time 15 as an adjustable and readable parameter. In preferred compositions that include rare earth chelates and chemical agents that act as lifetime modifiers, multivariable codes are produced for the purpose of tagging products or documents. The methods described will be well suited for 20 control of product inventory, and in measures that counter product diversion and counterfeiting.

The photoluminescent signal that constitutes a covert label under the preferred embodiments has a combination of innovative features. We summarize the important features of 25 the spectroscopic data as follows. As shown in Fig. 5 for europium and terbium chelates, luminescence occurs in relatively narrow lines that are better resolved than the fluorescence that is commonly observed for conventional dyes. Chelates show low absorptivity in the visible region, 30 so that marks are not visible to the naked eye. Luminescence can be observed by combining two dyes and using

derivatives of imidazole that serve as ancillary coordinating ligands, or coordinating polymers such as polyvinyl acetate), have been identified which can be used in conjunction with a variety of chelates in order to 5 produce a matrix of variables that include emission wavelength and decay time. It is further demonstrated that a combination of one or more dyes having variable lifetimes according to individual compositions of the marking ink can be scanned for recording wavelength and decay time with high 10 fidelity. Also described is a simple inexpensive detector that can be used for the collection, digitization, and communication of luminescence data.

Security features will display not only a physical image and a color (luminescence wavelength) upon 15 interrogation. A critical additional level of security is associated with "lifetime imaging" - i.e., a covert signature will also include a well defined luminescence decay time, a distinct but adjustable property of each chelate and the medium in which it resides. Lifetime 20 imaging is carried out using pulsed light excitation for sampling. The results of recording lifetimes for various samples are shown in Figs. 4 and 6. Luminescence lifetime data are compiled in Table 2 that show (see '891) the versatility of the method in terms of application of 25 different dye formulas having different lifetime modifiers to paper.

The success of lifetime imaging as a security feature depends critically on two factors: (1) the reproducibility of lifetimes for a given sample (the combination of chelate, 30 the medium with which it is applied, and the substrate); and (2) the ability to alter lifetimes in a systematic manner by

methylimidazole have been reported (W.J. Evans, et al., Chem. Commun., 2367 (1998); W. J. Evans, J. Coord. Chem., 34, 229 (1995)).

The new findings that are enabling have to do with the 5 systematic modification of lifetimes that can be brought about by addition of imidazole to chelate reagents (Table 2). The data in sum demonstrate that lifetimes can be modified typically 25-50% on the addition of an imidazole modifier.

10 Another interesting feature of the luminescence data is the subtle change in peak emission intensity that is observed for the principal lanthanide emission bands on addition of a coordinating group ("modifier"). For example, addition of imidazole brings about a change in the intensity 15 ratio. This determination is consistent with the finding that the electric dipole character for the $^5D_0 - ^7F_2$ band (612 nm) is more sensitive to the ligand field and can reflect the number of coordinating ligands of a particular type (G. Blasse, Adv. Inorg. Chem., 35, 319 (1990)).

20 A second class of modifier is most efficacious in situations in which a lanthanide chelate is applied via an organic solvent. This type of composition of security ink is most appropriate for marking materials comprised of conventional plastic (e.g., vinyl polymer or polyester).

25 The preferred modifier for this type of substrate is poly(vinyl acetate) (PVA), a well known commercial alkene polymer having a molecular weight in the range of 10,000 - 500,000 Da (K. J. Saunders, "Organic Polymer Chemistry"). We have demonstrated that for europium chelates that employ 30 ligands of the 1,3-diketone class, the luminescence intensity (in the absence of an additive) is reduced and

having metal oxide or metal sulfide structures. Examples of these pigments that absorb ultraviolet light and emit light in the visible range include composites of zinc sulfide and copper or manganese (e.g., ZnS:Cu) (or yttrium-europium structures (e.g., Y₂O₃:Eu)). These compounds give rise to luminescence that displays decay times of 0.3 to 25 ms when they are applied to paper or label stock with a suitable dispersant (e.g., poly(vinyl acetate), PVA).

In addition to the dyes disclosed in '891, it has been found that any luminescent dyes, or pigments, can be used herein. When one considers that there are virtuallyy unlimited number of possible sizes and shapes of the "printed" version of each dye (see '891), including each dye being printed in the shape of a letter or number, one realizes the number of permutations. In addition, the concentration of dye (i.e., amount of dye per surface area) can be varied, in order to vary the amplitude of the signal. If more than one dye is used, the relationship (e.g., ratio) between concentration of the dyes is another variable. Having the ability to utilize such a large number of combinations of dyes, plus the ability to frequently change the combination and communicate identification to those who need to authenticate products/documents provides a system that is extremely difficult to counterfeit.

Consider the attached Diagram as depicted in Figure 7. The signaling and data paths commence with the Power Supply 1 that provides the electrical excitation for the optical source, and may also provide power to other electrically-powered elements of the optical component, generally an optical scanning unit, which consists at least in part of a Scanner system such as the Scanning element,

spectral range that may include, but is not limited to, UV and visible wavelengths.

The Delivery Path 3 consists of a fiber or fiber bundle, a lightpipe, any other type of optical waveguide, 5 air or some other medium, and/or free space optics such as lenses. The Delivery Path spatially (and spectrally) formats and efficiently transmits the excitation light to optimally excite the Mark.

The Mark 4 may consist, for example, of luminescent 10 dye(s) and/or inks formulated with luminescent dyes, capable of producing an emitted optical spectrum under optical excitation. The Mark may be a thin film, barcode, 1-D or multidimensional barcode, marking thread(s), or labels. The Mark may be printed by a variety of methods, including, but 15 not limited to, ink jet, thermal transfer, dye sublimation, or screen printing. The Mark may be incorporated in a label, card, foil or part, (e.g., dye incorporated as a dopant in plastic label or card stock or adhesive, or foil), in fabric or in thread. The Mark may be applied with a 20 laminant layer or incorporated into an adhesive layer. The Mark may be applied to packaging: for example, as pharmaceutical packaging such as boxes, plastic wrap, bottles, and/or bottle caps.

The Mark may incorporate one or more spatially-distinct 25 areas that incorporate luminescent dyes, said dyes and their deposition being described in '891. The Mark may alternatively incorporate two or more spatially overlapping areas that incorporate fluorescent dyes, said dyes described in '891. The Mark may incorporate two or more spatially 30 overlapping areas that are coextensive that incorporate luminescent dyes, said dyes described in '891. The Mark

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The Emission Filter may incorporate several of these filters, for example in a filter wheel. The Emission Filter must pass spectral power in the emission wavelength bands of the Mark luminescence. The Emission Filter may pass 5 wavelengths in some subset(s) of the UV, visible, and infrared portions of the spectrum.

The light that passes through the Emission Filter may be further formatted spatially by a Scanning element. This Scanning element may consist of a holographic, galvanic, 10 electro/optic, MEMS, or other transmission or reflective scanning element or elements, and may be scanned in 1-D or 2-D. Similarly, the light from the Source may be optionally scanned in this fashion.

The Detection element(s) 7 convert the emissive 15 output(s) of the Mark into electrical signal(s). The Detection element may consist of one or more discrete detectors such as PMTs; silicon, GaAs, AlGaN, InGaAs, or similar optical semiconductor detectors; bolometers; a multiplicity of these detectors in a linear or 2-D array; or 20 a multiplicity of semiconductor detectors such as are found in a linear or 2-D CCD or CMOS arrays. The choice of detector(s) is determined by the amplitude, speed, signal-to-noise ratio, and spectral bandwidth of the Mark's emission(s). These may have integral amplification. The 25 Detection means may be synchronous or asynchronous with the Source's modulation and/or triggering.

The Electronics 8 may consist of one or more preamplifiers, lock-in amplifier(s), wide-band noise rejection filter(s), narrow-band electrical filter(s), other 30 analog signal conditioning, timing and gating sources, triggering outputs and inputs, and may also include one or

uploaded to the Scanner via some external Data Link, or may be stored at some remote location (in this last embodiment, a "compressed" version of the raw data from the fluorescence emission, such as a table of fluorescence decay lifetime(s), 5 would be transmitted over the Data Link to a Remote Host). A block diagram illustrating the processing scheme is found in Figs 9 and 10.

In another embodiment of the system, the information modulated by the Mark and measured by the Scanner is the 10 Mark's selective influence on the known input polarization state of the Excitation Spectrum. For example, the plane polarization state of the excitation light may be rotated with respect to the polarization of the emission from the 15 Mark. The amount of rotation is affected by the alignment of the Mark dye molecules and the length of the emission decay time. This provides another unique "signature" for the Mark that also may be used for authentication: the time-resolved polarization state of the emission spectrum.

Upon the completion of this comparison, the Scanner's 20 Display (9 in Figure 7) would provide the user with an indication, for example, of whether or not a Mark was detected, and whether this Mark was "authentic". The Display can also provide the user with an indication of the system's status, power on/off, etc. The Display can consist 25 of an LCD readout, CRT, one or more LEDs of one or more color, incandescent lights of one or more color, or some combination of these elements. The Display may be augmented by an audible output that can provide another means of alerting the user to the aforementioned indications.

30 The Scanner can optionally incorporate a Data Storage element. This can consist of an EPROM, ROM, RAM, or other

Emission Filter, the Scanning element (as necessary), the Detection element, and the Electronics (Fig. 11). In such a configuration, the Scanner can even be hand-held. One likely embodiment would be an imaging Scanner which both 5 detects, landmarks, image processes, and authenticates the Mark. Another embodiment would further include the balance of the elements outside of the Remote Host block within a hand-held unit. These two Scanner embodiments may be fixed in space, and mounted on or near a conveyor system to 10 automatically scan products as they pass the fixed Scanner. In this embodiment the time signature may be detectable using two or more adjacent Detection elements or Scanners, with the spatial separation between these elements effectively "scanning" the Mark where, rather than the 15 excitation spectrum being spatially scanned over the Mark, the Mark moves with respect to a fixed spatially-formatted excitation "beam".

The information technology component used herein (typically a computer) must be capable of analyzing all of 20 the potential systems being evaluated by the system. If the system is being utilized by an organization that must authenticate many products or documents, both the scanner and information system must be capable of detecting many dyes and must be capable of storing information on the 25 authentication characteristics for many products. As indicated, the authentication system must be capable of changing the dyes at any time in order to reduce the likelihood that counterfeiters can "break the code" and create a substitute label system. Therefore, the 30 information technology must be capable of receiving periodic input, either via computer disk, eMail transmission,

significant activity takes place (for example, adding important information to a document or exposing the product to a special treatment, such as exposure of the product to sterilizing radiation). Alternatively, the information to 5 be coded can be accumulated and all applied at the same time.

Another variation deals with the relationship between the spectral characteristics of the dyes. For example, the ratio of amplitude of the dyes at their maximum emission 10 wavelength can be the characteristic used to determine authentication. Yet another variation can be employed in a forensic application, as follows. Two or more dyes may be used in combination such that detection of luminescence at two wavelengths is possible. A sample can be recorded with 15 regard to a ratio of peak intensities or decay times before placement in the field. On return, the item can be interrogated again, following a pre-treatment with heat or light (electromagnetic radiation) or washing. With proper dye selection, there will be a selective degradation of dye 20 by the pre-treatment, leaving part or all of a remaining dye substance that will reveal a unique "before and after" luminescence, or signature. Such variations in spectral characteristics can also be evaluated and reported by the information technology system. Examples of treatments that 25 can be used include:

1. heating tagged samples in a drying oven before spectral analysis (approximately 10 minutes to 24 hours at 50-250 C.),
2. irradiating tagged samples before spectral 30 analysis using lamps that include, but are not limited to, xenon, halogen, or mercury, or laser sources that include

functions, and a statistical analysis of goodness-of-fit to the decay data.

In another embodiment, the comparison of luminescence may be carried out using devices of simple design that allow 5 portability and ease of operation by personnel having minimal training in the field of luminescence spectroscopy. For example, a compact, hand-held apparatus (see Fig. 13) can be fabricated that incorporates a readily available emitting diode light source, and inexpensive diode detector, 10 and simple circuitry that can be understood and implemented by persons skilled in the art of detector electronics. Such a device is illustrated in the description of a UV-scanning apparatus, constructed from available optical and electronic components, that has the capability of discriminating slow- 15 decaying luminescence. These components include a very low-leakage Hamamatsu photodiode (R2506-02), a high impedance (10-12 Ohm) FET operational amplifier (TLO 64), CMOS analog switches (74HC 4066), and a MOSFET low on resistance transistor (IRF 7503) for UV modulation. Utilizing a double 20 differential scheme, the apparatus is relatively insensitive to ambient light and/or temperature changes. Extremely weak signals of luminescence can be sensed by the low-leakage photodiode, if signals are amplified and averaged over multiple periods of the clock generator to improve the 25 signal/noise ratio.

In another embodiment of the present invention, the coding of luminescence information is detected using a scanning device that can store or transmit data for recovery and use in the verification of product or document identity. 30 The storage and transmission of data for recovery may be accomplished via any type wired or wireless communication,

black/white ink jet cartridge and printed on plain white paper stock and on a variety of different surfaces of commercial paper packaging. Dyes labeled # 5 (green emission, short wavelength UV), and # 6 (red emission, short wavelength UV) were also used. All of these ink jet printed compositions showed bright luminescence under the respective UV illuminations and provided well resolved spectral images of a variety of printed 1D and 2D bar codes.

In this embodiment, the covert barcode emits luminescence with unique spectral, spatial and temporal properties. The emitted light is collected, filtered, and focused onto a standard silicon photodiode detector. This generated signal is then integrated and processed by associated electronics, and sent to a display. In the prototype, the display was provided by a digital oscilloscope which clearly showed the unique characteristic timestamps of the invisible barcodes. The output of the oscilloscope display was digitally captured and appears in Figure 4. From this decay curve a luminescence decay time was recorded ($\tau = 1.2 \text{ ms}$).

Example 3.

Another embodiment of the invention has been prototyped in a handheld "yes/no" digital lifetime detector. This embodiment is shown schematically in Figure 13. The device is intended to identify arbitrary marks (e.g., barcodes) that are based on the unique luminescent compounds (e.g., europium or terbium chelates) and chemistries described herein. This capability is enabled by specifically designed excitation and emission optics that are "tuned" to the bands of the luminescent compounds, and appropriate signal processing electronics

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recording or transmitting to a remote location. The handheld prototype has been used to successfully interrogate dyes of the type described in this application, which have been ink-jet printed on standard white paper as a covert
5 barcode.

Example 4.

In this example, forensic chelate samples were heat treated. Samples of a polyester film were coated with a mixture of dyes in a styrene-acrylic resin (Joncryl 67 and
10 678, [trademark of S. C. Johnson]). In this preparation proprietary dye substances labeled I and II were dispersed together at a concentration of 0.5% w/v in a methyl ethyl ketone solution of resin (5% w/v). The coatings were accomplished by drawing down a film using a # 24 Meyer rod.
15 Samples were air dried for 30 minutes before placement in a laboratory drying oven that was equilibrated at 105 C. Samples of film were harvested at 24 hour intervals and cut to an appropriate size for analysis using a PTI fluorimeter. The luminescence spectra recorded for samples obtained after
20 three 24-hour heat treatment intervals are shown in Fig. 14 (untreated sample, upper left; sample after 3 days, lower right). Graph (a) shows both dyes (the one that absorbs at 612 nm and the one absorbing at 618 nm) at the beginning of the heat treatment process. Careful scrutiny showed that
25 the dye, I, that emits with a peak at 612 nm is selectively degraded by heat treatment such that the sample after the 3-day trial corresponds to the emission of dye II (peak luminescence at 618 nm, lower right). Also noticeable was the change in luminescence decay time (inserts, Fig. 14);
30 pre-treatment (Fig. 14a) lifetime readings having the shorter times associated with a combination of luminescence

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CLAIMS

1. A system for product or document authentication, said system comprising:
 - 5 a. one or more luminescent or fluorescent tags, said tags being applied to said product or document,
 - b. an optical scanning component for detecting a signal emitted by said tag, and
 - c. an information technology component for analyzing 10 said signal.
2. The system of claim 1 wherein at least one of said tags has an emitted signal of known time resolution.
- 15 3. The system of claim 2 wherein said known time resolution is the time to decay to a predetermined value.
4. The system of claim 1 wherein at least one of said tags is a mixture of more than one compound.
- 20 5. The system of claim 2 wherein at least one of said tags is selected from the group consisting of dyes, inks and pigments.
- 25 6. The system of claim 4 wherein one of said tags is a mixture of a luminescent compound and a luminescence lifetime modifier.
7. The system of claim 6 wherein said luminescent compound 30 is a lanthanide chelate.

15. The information technology component of claim 13 in which said further analysis also includes the determination of whether said tag is authentic.

5

16. The system of claim 1 in which said optical scanning component comprises a light source, tag, scanner, and information technology system.

10 17. The system of claim 1 in which said tags are applied at different times.

18. The system of claim 1 in which said tags are applied at the same time.

15

19. The system of claim 1 comprising two or more luminescent or fluorescent tags, at least one of said tags being a mixture of a lanthanide chelate and a luminescence lifetime modifier.

20

20. The system of claim 1 comprising two or more tags.

21. A system for product or document authentication, said system used to detect the presence of one or more 25 luminescent or fluorescent dyes, wherein said dyes are applied to said product or document, and wherein said system comprises:

- a. an optical scanning component for detecting signals emitted by said dyes, and
- 30 b. an information technology component for analyzing said signals.

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26. The method of claim 25 in which at least one of said tags has an emitted signal of known time resolution.
27. The method of claim 25 in which the time for said tag to decay to a predetermined value is known.
5
28. The method of claim 25 in which at least one of said tags is invisible to the human eye.
- 10 29. A method for product or document authentication, said method being used to detect the presence of one or more luminescent or fluorescent dyes, wherein said dyes are applied to said product or document, and wherein said method comprises:
 - 15 a. using an optical scanning component for detecting signals emitted by said dyes, and
 - b. using an information technology component for analyzing said signals.
- 20 30. A method for product or document authentication, said method being used to detect the presence of two or more dyes used as tags for said product or document, the combination of said dyes yielding a unique identifier, wherein said method comprises:
 - 25 a. treating said tagged samples by exposing them to elevated temperature, electromagnetic radiation, or washing with selected solvents,
 - b. using an optical scanning component for detecting dye luminescence, and
 - 30 c. comparing said dye luminescence detected vs. control samples treated by similar exposures to elevated

38. A method of claim 30 in which dye tagged samples are washed before spectral analysis with solvent.

5 39. The method of claim 38 wherein said solvent is selected from the group consisting of acetone, tetrahydrofuran, chlorocarbon, ethyl acetate, toluene, dimethyl sulfoxide, dimethylformamide, water and mixtures thereof.

10 40. A composition of metal chelates in which the metal center is coordinated to one or more ligands that display charge transfer absorption bands.

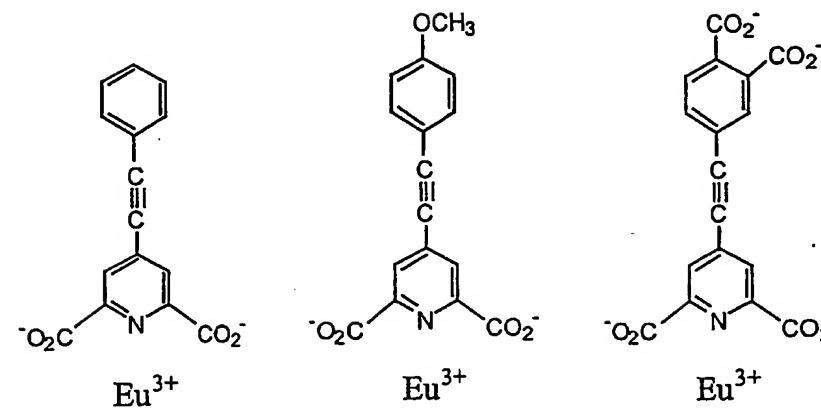
15 41. A composition of chelates of claim 40 in which the metal center is a lanthanide element, including but not limited to the elements, europium, terbium, samarium, neodymium, gadolinium or ytterbium.

20 42. A composition of chelates of claim 40 in which the ligand is composed of aromatic rings having electron donating substituents.

25 43. The composition of claim 42 wherein said electron donating substituents are selected from the group consisting of -OH, -OR, -O⁻, -NH₂, -NR₂, -NHR, -CO₂⁻, -SO₃⁻ and -SR.

44. A composition of chelates of claim 40 wherein said ligand is composed of aromatic rings having electron withdrawing groups.

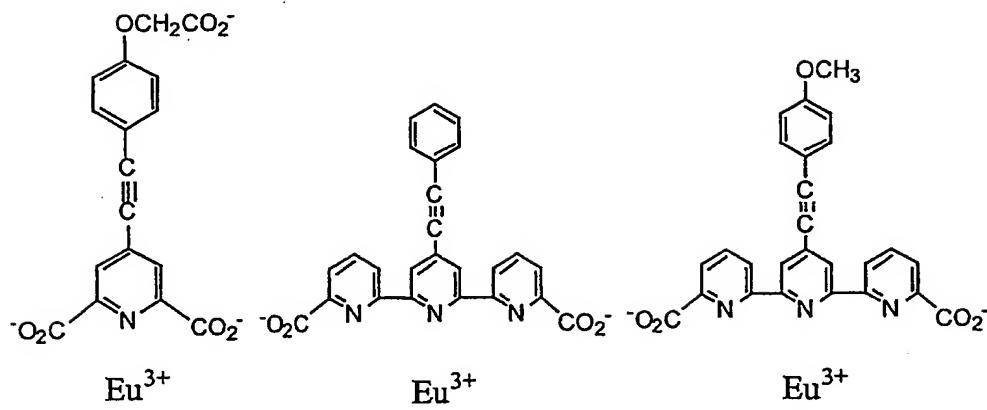
1/17



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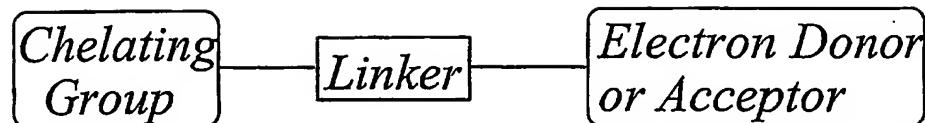
4

5

6

Figure 1

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Example:

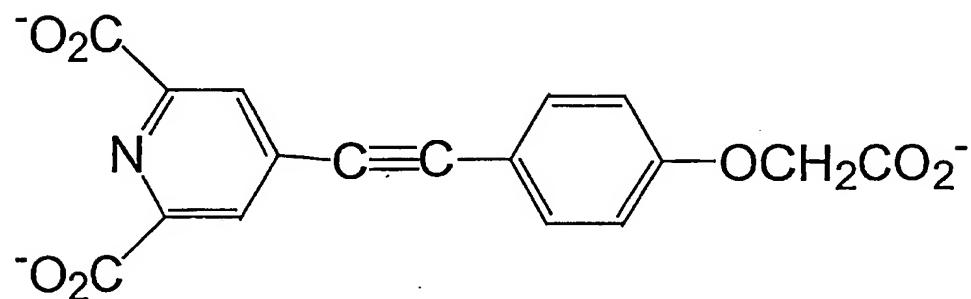


Figure 3

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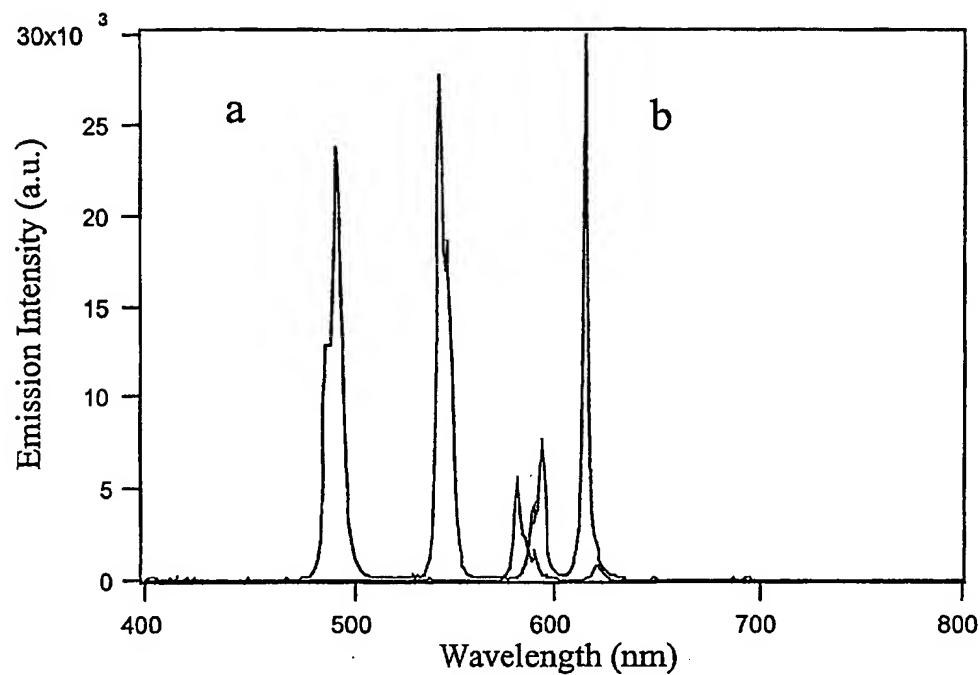


Figure 5

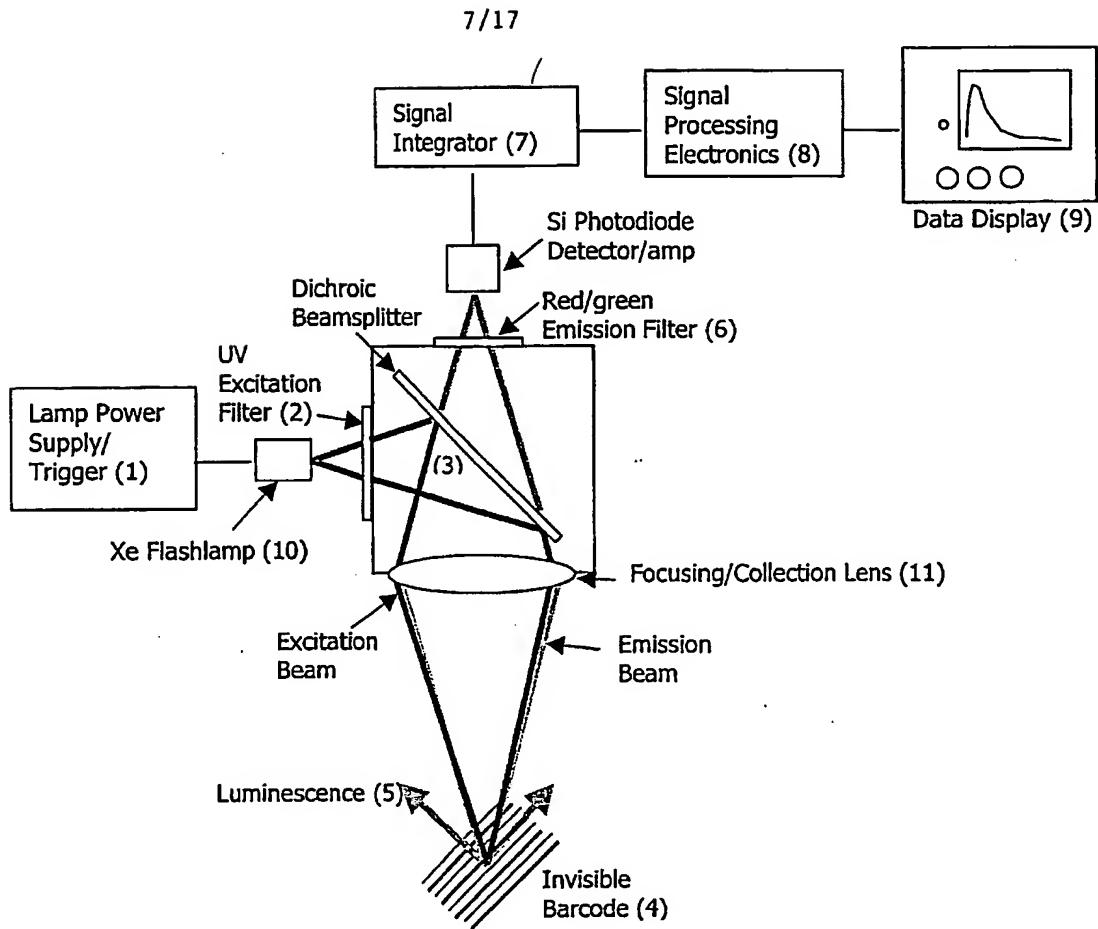


Figure 7

System Operation

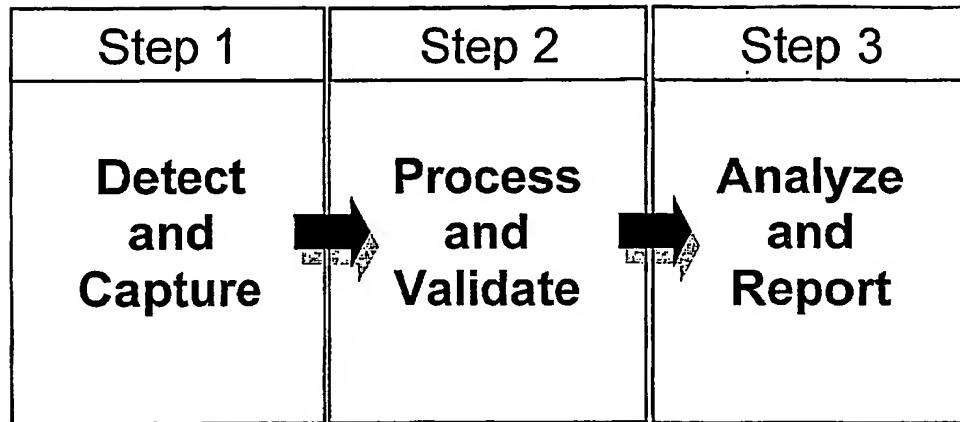


Figure 9A

Step 2 Process and Validate

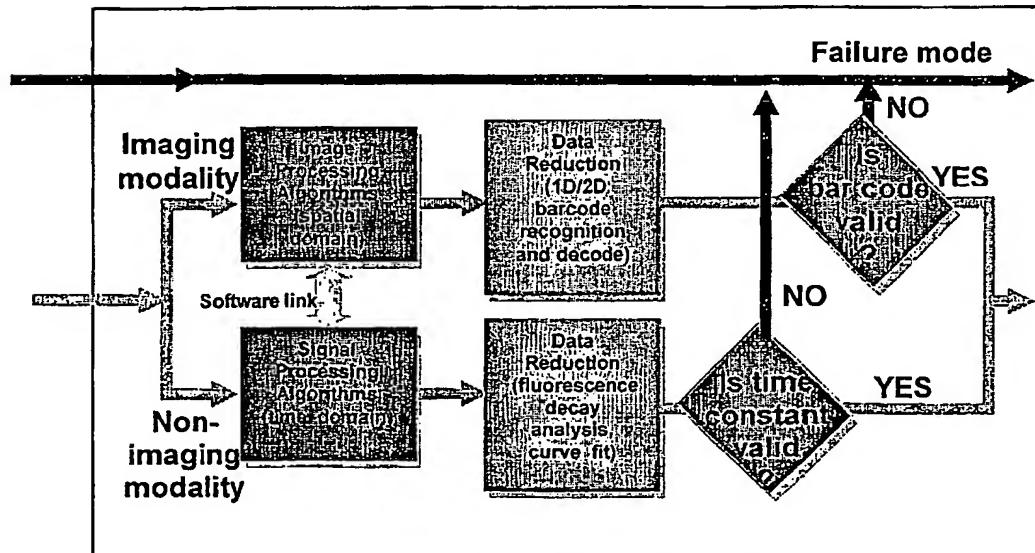


Figure 9B

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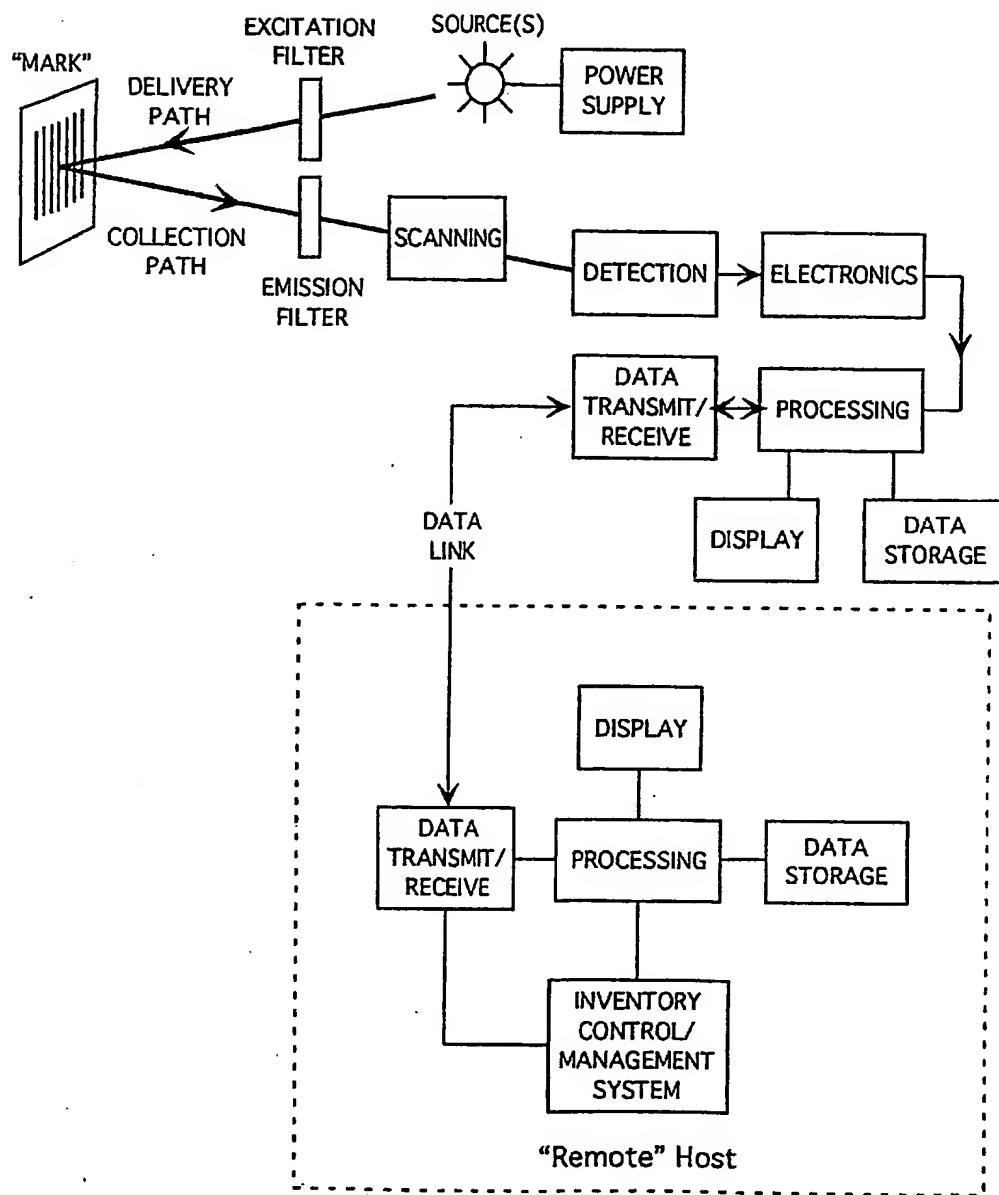
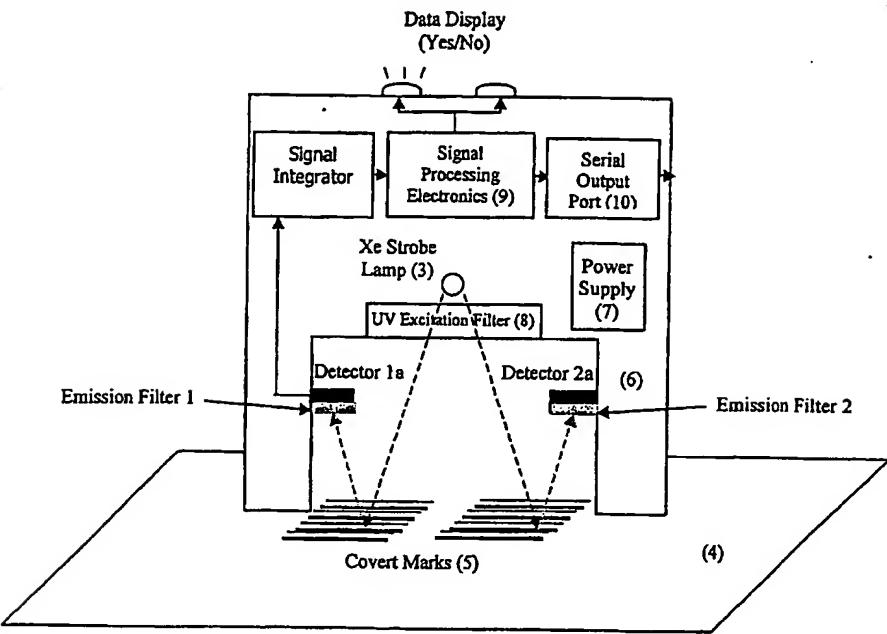


Figure 11

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**Figure 13**

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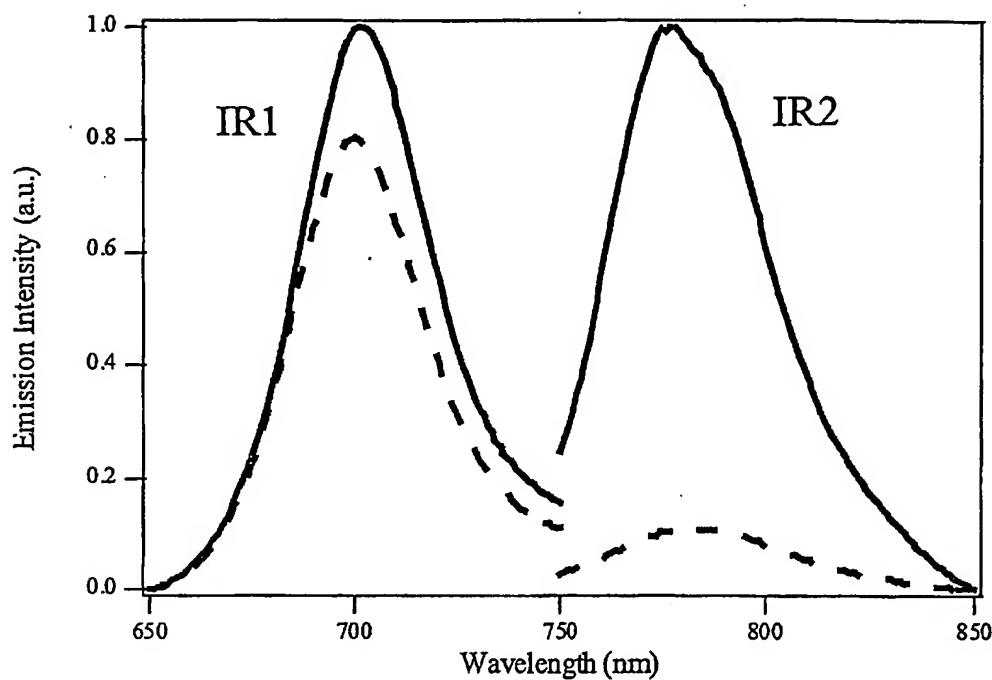


Figure 15

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Table 2 Luminescence lifetime data for chelates

Chelate	Modifiers ^a			
	None	Imidazole	4-MI	IDA
1	0.97 ms	1.19 ms	1.22 ms	0.45 ms
2	1.02 ms	1.21 ms	1.37 ms	0.48 ms
3	1.01 ms	1.23 ms	1.19 ms	0.46 ms
4	0.97 ms	1.27 ms	2.03 ms	0.60 ms
5	0.36 ms	0.65 ms	0.54 ms	0.50 ms

a, Modifiers at 1.0 mM concentration; Imidazole, 4-methylimidazole (4-MI), and iminodiacetic acid (IDA), were added to an application medium of 200 µM chelate in water (pH9.0) and applied to plain paper; lifetimes (units' of ms) from exponential luminescence decay curves ($\lambda_{\text{exc}} = 337 \text{ nm}$; $\lambda_{\text{lum}} = 615$).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/17868

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,283,382 A (FRANK et al) 11 August 1981 (11.08.1981), column 1, lines 39-52.	42-45

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